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OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 10/11/80

Project Title: Research into Methods of Synthesizing Selected Macrocyclic Polyethers (Crown Ethers)

Project No: G-33-671

Project Director: Dr. Charles L. Liotta

Sponsor: Union Carbide Corporation, Nuclear Division, Oak Ridge, TN 37830

Agreement Period: From 7/7/80 Until 6/30/81

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SPONSORED PROJECT TERMINATION SHEET

Date 6/2/83

Project Title: The Synthesis of Selected Macrocyclic Polyethers(Crown Ethers)

Project No: G-33-671

Project Director: Dr. Charles L. Liotta

Sponsor: Union Carbide Corp.

Effective Termination Date: 6/30/81

Clearance of Accounting Charges: 6/30/81

Grant/Contract Closeout Actions Remaining:

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- [ ] Final Fiscal Report
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- [X] Govt. Property Inventory & Related Certificate
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Assigned to: Chemistry (School/~~Laboratory~~)

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FORM OCA 10:781

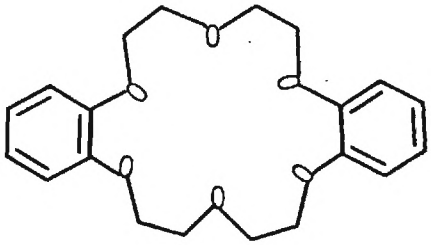
FINAL REPORT: G-33-671

THE SYNTHESIS OF SELECTED MACROCYCLIC POLYETHERS (CROWN ETHERS)

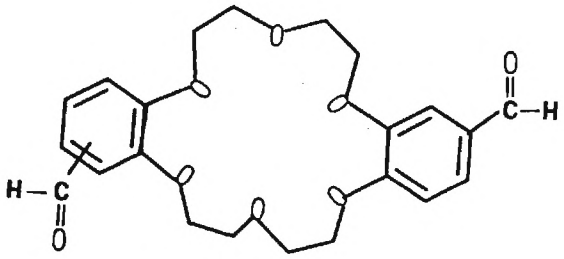
Charles L. Liotta
School of Chemistry, Georgia Institute of Technology

The following macrocyclic polyethers have been synthesized for

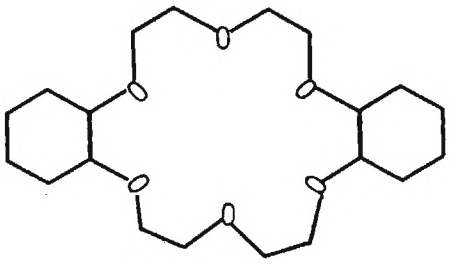
"Study of the Size Selective Extraction of alkali metal Ions by the Synergistic Extraction System, Crown Ether-Di-(2-ethylhexylphosphoric) Acid-Benzene."



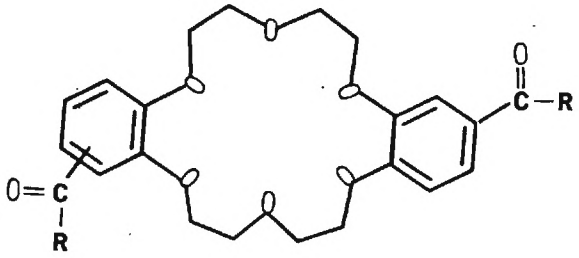
Dibenzo-18-crown-6



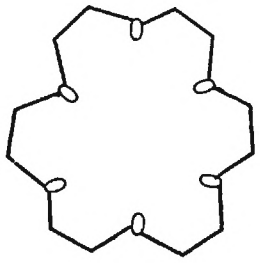
Diformyldibenzo-18-crown-6



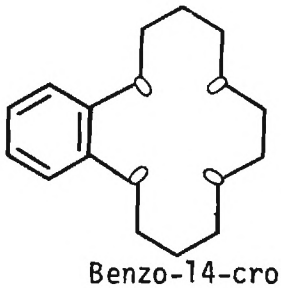
Dicyclohexyl-18-crown-6



Dialhyloyldibenzo-18-crown-6



18-crown-6



Benzo-14-crown-4

Experimental

Dibenzo-18-crown-6

A dry 5-l three-neck flask is fitted with a reflux condenser, a 500-ml. pressure-equalizing dropping funnel, a thermometer, and a mechanical stirrer. An inlet tube at the top of the condenser is used to maintain a static nitrogen atmosphere in the reaction vessel throughout the reaction. The flask is charged with 330g. (3.00 moles) of catechol and 2l. of 1-butanol and then stirring is started and 122g. (3.05 moles) of sodium hydroxide pellets is added. The mixture is heated rapidly to reflux (about 115°) and then a solution of 222g (1.55 moles) of bis(2-chloroethyl) ether in 150 ml. of butanol is added, dropwise with continuous stirring and heating, over a 2-hour period. After the mixture has been refluxed for an additional hour, it is cooled to 90° and an additional 122g. (3.05 moles) of sodium hydroxide pellets is added. The mixture is refluxed for 30 minutes and then a solution of 222g. (1.55 moles) of bis(2-chloroethyl) ether in 150 ml. of butanol is added, with stirring and heating, over a 2-hour period. The final reaction mixture is refluxed, with stirring, for 16 hours and then acidified with 21 ml. of concentrated hydrochloric acid. The reflux condenser is replaced with a distillation head and approximately 700 ml. of butanol is distilled from the reaction mixture. As the distillation is continued, water is added to maintain a constant volume in the flask. The distillation is continued until the distilling vapor exceeds 99 and then the resulting slurry is cooled to 30-40°, diluted with 500 ml. of acetone, stirred to coagulate the eprcipitate, and filtered with suction. The crude product is stirred with 2l. of water, filtered with suction, stirred with 1l. of acetone, and again filtered with suction. The residual product is washed with an additional 500 ml. of acetone and then sucked dry. This product, tan fibrous crystals melting at 161-162°, amounts to 221-260g.(39-48%) and is sufficiently pure for use in the preparation of dicyclohexyl-18-crown-6.

The product may be purified further by recrystallization from benzene. The dibenzo-18-crown-6 separates as white fibrous needles melting at 162.5-163.5°. The product has ultraviolet maxima (methanol solution) at 223 mμ (17,500) and 275 mμ (5500) with n.m.r. peaks (CDCl solution) at 6.8-7.0 (8H multiplet, aryl CH) and 3.8-4.3 p.p.m. (16H multiplet, CH -O). The mass spectum exhibits the following peaks: m/e(rel.int.), 360 (M+,29), 137(29), 136(74), 121(100), 109(23), 80(31), 52(21), 45(27), and 43(34).

Diformyldibenzo-18-crown-6

A dry 1-l. three-neck flask is fitted with a mechanical stirrer, 100-ml. addition funnel, and a nitrogen inlet tube. The flask is charged with 20g. (0.056mole) of dibenzo-18-crown-6 and 500ml. of 1,2-dichloroethane. The mixture is cooled using an ice bath and maintained at this temperature throughout the additions. The dropping funnel is charged with 61.6-ml. (0.56 mole) of titanium tetrachloride. The titanium tetrachloride is added over a period of 30 minutes. After the resulting mixture has stirred for an additional 30 minutes, 20.3-ml (0.22 mole) of α, α dichloromethylmethyl ether is added over a ten minute period. The solution is then allowed to warm to room temperature and stir overnight. The dark red solution is poured onto 1 l. of an ice-water mixture. The aqueous phase is extracted with methylene chloride. The organic layer is filtered through a two inch pad of silica gel resulting in a clear yellow solution. The solvent is removed by rotoevaporation resulting in a yellow solid. The solid is dissolved in ethyl acetate, decolorizing carbon is added and the mixture is refluxed for 30 minutes. White crystals are obtained after filtering through celite and removal of the solvent. Typical yields are around 25%. Decomposes at 160.

Dicyclohexyl-18-crown-6 A 1-l stainless steel autoclave is charged with a mixture of 125g. (0.347 mole) of dibenzo-18-crown-6, 500 ml. of freshly distilled butanol, and 12.5g. of 5% ruthenium-on-alumina catalyst. After the autoclave is closed, it is flushed with nitrogen and filled with hydrogen. The mixture is hydrogenated at 100 and a hydrogen pressure of 700 atm. (1000 p.s.i.) until the theorectical amount of hydrogen (2.08 moles) has been absorbed. The autoclave is cooled to room temperature and filtered to remove the catalyst. The filtrate is concentrated under reduced pressure at 90-100 with a rotary evaporator. The residual product solidifies on standing. To remove hydroxylic impurities, a solution of the crude produce (about 130g) in 400 ml. of n-heptane is filtered through a 7-cm. by 20-cm. column of acid-washed alumina (80-100 mesh, activity 1-2), and the column eluted with additional n-heptane until the eluate exhibits hydroxyl absorption in the 3- region of the infared. The solvent is removed from the combined eluates with a rotary evaporator to leave 75-89g (58-69%) of mixture of diastereomeric dicyclohexyl-18-crown-6 as white prisms melting within the range of 38-45. The n.m.r. peaks (C D solution) 3.3-4.0 p.p.m. (20H multiplet, O-CH) and 0.9-2.2 p.p.m. (16H multiplet, aliphatic CH). The mass spectrum peaks: m/e(rel.int), 372(M+,2), 187(35), 143(100), 141(47), 99(92), 18(46), 97(41), 89(66), 87(41), 83(45), 82(55), 81(99), 73(77), 72(46), 69(58), 67(42), 57(50), 55(58), 45(77), 43(61), and 41(58).

The syn and anti isomers of dicyclohexyl-18-crown-6 can be separated by the following method. The isomer mixture of dicyclohexyl-18-crown-6 (10g) is added to 1l. of distilled water at 60. After the cyclic ether meltes, the mixture is allowed to cool to room temperature with vigorous stirring. The dissolution takes 10-20 hours. A solution of lead perchlorate,

prepared by dissolving 14.4g of lead carbonate in a mixture of 14.8g of 70% perchloric acid and 15 ml. of water, is then added to the ether solution which is stirred for an additional 60 minutes to complete crystallization. The resulting lead perchlorate comples of the anti isomer is filtered to yield 9.7g of colorless crystals. The filtate contains the syn isomer.

The lead perchlorate complex is dissolved in 60 ml. of N, N-diethylformamide. Water (60 ml.) is added to this solution and hydrogen sulfide gas is bubbled through it until precipitation of lead sulfide is complete. Immediately thereafter, 60 ml. of acetone is added, the PbS is filtered off, and the solvents are removed from the filtrate under vacuum. To the resulting viscous oil is added 60 ml. of water, and this mixture is extracted with three 250-ml portions of n-hexane. The combined n-hexane extracts are dried over anhydrous magnesium sulfate and filtered. The n-hexane is removed under vacuum, and the solid is recrystallized from n-hexane. The yield is 3.9g. (39%) of colorless crystals of the anti isomer, mp 83-84.

The filtate which contains the syn isomer is treated with hydrogen sulfide gas until the precipitate of lead sulfide is complete. The solid PbS is filtered off, and enough 70% perchloric acid (about 45 ml.) is added to the filtate to start the precipitation of the oxonium complex of the syn isomer. The solution is stirred for 15 minutes and an additional 15 ml. of 70% perchloric acid is added to ensure complete precipitation of the solid. The mixture is stirred for an additional hour and then filtered to yield 6.4g. of the colorless crystals of the oxonium perchlorate complex. The oxonium comples is dissolved in 50 ml. of acetone and then 150 ml. of

water is added. The solution is extracted with n-hexane, dried over anhydrous magnesium sulfate and filtered. The n-hexane is removed under vacuum, and the solid is recrystallized from n-hexane or diethyl ether to yield 4.4g. (44%) of colorless crystals of the syn isomer, mp 61-62.

Acylation of benzo crown ethers

Preparation and standarization of the condensensing reagent

A mixture of 83g. of phosporic pentoxide and 695 ml. (1030g) of methanesulfonic acid, anhydrous, was stirred until all of the solids were dissolved (about 36h). A mixture of 3.6g. (0.01 mole) of dibenzo-18-crown-6, 1.2g. (0.02 mole) of acetic acid, and 13g. of the condensing agent was stirred for 6h. The reaction mixture was worked up in the usual manner (see below). The n.m.r. spectrum of the crude product showed 50% reaction had occurred. It was therefore assumed that 13g. of the condensing agent was required to bring about the condensation of 0.01 mole of carboxylic acid, and this figure was used in determining the optimum amount of condensing reagent to use in all subsequent reactions.

Bis (4' (5')-acetylbenzo)-18-crown-6

A mixture of 0.02 mole of dibenzo-18-crown-6 and 0.042 mole of acetic acid was dissolved in 54.6g. od condensing agent and stirred for 6h. The reaction mixture slowly turned dark red. The mixture was poured onto 100 ml of water, neutralized with sodium bicarbonate, and extracted three times using methylene chloride. The organic extracts were combined, washed with water, and dried over sodium sulfate. The solvent was removed to yield a light tan solid, 86%. The solid can be recrystalized from ethyl acetate to yield white crystals, mp 200-208.

18-crown-6

A 3-necked round-bottom flask, fitted with an efficient mechanical stirrer, a reflux condensor, and a 250-ml addition funnel is charged with 85% potassium hydroxide pellets (416g, 6.3 moles) and THF (1 liter). After about 15 minutes, the bis (2-chlorethyl) ether (366.4 ml, 3.13 moles) can be added. Initially about 50 ml. of the ether is added and about a 15 minute induction period occurs before the solution heats up. After the solution has stopped refluxing, the ether can then be added dropwise to maintain reflux. When the addition is complete, heat is applied to the flask to maintain reflux for an additional 18 hours. The solution is cooled and the solvent is removed under reduced pressure to yield a brown slurry to which 750 ml. of dichloromethane is added. The resulting mixture is filtered and the residue is washed with 100 ml. of dichloromethane. The combined filtrate and washing is dried with magnesium sulfate, filtered and the solvent is removed under reduced pressure. The viscous liquid is then distilled to give a colorless liquid (215g), bp 110-210 /0.02 torr. Sometimes the liquid is slightly discolored. The liquid is dissolved in acetonitrile (500 ml.) and the solution is cooled to -45° (methanol/Dry Ice bath). The resultant precipitate of 18-crown-6-acetonitrile complex is collected by filtration. Removal of the acetonitrile by vacuum yields 100g. (30%) of 18-crown-6, mp38-38.5, bp 116/0.2 torr.

Preparation of Bis (2-cyanoethoxy)ethane[10]

Into a 1 liter, 3-necked flask equipped with a stirring bar, addition funnel and internal thermometer were placed ethylene glycol (124g, 2.00 moles) and a solution of 2g of KOH in 3 ml of water. Acrylonitrile (213g, 4.00 moles) was allowed to slowly drip in from the addition funnel while

the temperature of the reaction mixture was maintained below 35°C with a cool (15-20°) water bath. When the addition was complete the reaction was allowed to stir overnight (ca. 18 hr) at room temperature. The resulting reaction mixture was a viscous brown liquid. After neutralization with 6 M HCl the reaction mixture was dissolved in methylene chloride causing a solid, presumably KCl, to precipitate. Drying with $MgSO_4$ followed by filtration and rotary evaporation gave the crude product as a brown viscous liquid. Distillation from 135-170° (0.2-0.3 mm) gave 248g of a colorless liquid. The residue from the distillation was transferred to a smaller flask and distilled to yield 35g of an amber liquid at 147-170° (0.1 mm). Redistillation of the combined distillates yielded 272g (81%) of the product as a clear colorless liquid; b.p. 135-155° (0.1 mm). nmr ($CDCl_3$) δ 2.63 (t, 4H), 3.67 (s, 4H), 3.73 (t, 4H), IR (neat), 2250, 1050-1150 cm^{-1}; mass spectrum m/e (rel. intensity), 168 (expanded scale M^+), 141 (4), 98 (11), 97 (11), 84 (35), 54 (100), 45 (18), 31 (18).

Preparation of Bis (2-carboxyethoxy)ethane[11]

Bis (2-cyanoethoxy)ethane (270g, 1.60 mole) was stirred with 640 ml of concentrated HOl (6.4 mole) in a 3 liter flask equipped with a mechanical stirrer and reflux condenser. The reaction mxiture spontaneously heated itself to 98° at which time a solid, presumably NH_4Cl, precipitated. When the temperature of the reaction fell to 70°C external heating was applied to maintain the temperature between 70 and 80° for about 3.5 hours. After cooling, the entire reaction mixture was evaporated to dryness in vacuo and the residue was then taken up in acetone. The white solid was filtered and washed with acetone. The combined acetone portions

gravity filtered and concentrated to give 316g (96%) of a golden syrup. nmr ($CDCl_3$) δ 2.58 (t, 4H), 3.55 (s, 4H), 3.73 (t, 4H), 10.23 (s, 2H); IR (neat) 3675-2300 (s), 1710-1740 (s).

Preparation of Bis (2-carboethoxyethoxy)ethane

Bis (2-carboxyethoxy)ethane (316g, 1.53 mole) was dissolved in 1500 ml of absolute ethanol and several drops of H_2SO_4 were added. This solution was allowed to stir under reflux overnight, protected from external moisture by a drying tube. After cooling the solution was neutralized by the addition of solid $NaHCO_3$ and stirred for about an hour. After filtration the ethanol was removed by rotary evaporation to give 365g of crude product. Distillation gave, after a small forerun, the purified ester boiling at 145-155° at 0.5 mm. The yield was 227g (1.15 mole) or 75%. nmr (CCl_4) δ 1.23 (t, 6H), 2.47 (t, 4H), 3.52 (s, 4H), 3.67 (t, 4H), 4.10 (quartet, 4H), IR 2980, 2870, 1730, 1370, 1350, 1250-1120 cm^{-1}; mass spectrum m/e (rel. intensity; M^+ not visible, 131 (22), 101 (34), 99 (47), 73 (52), 59 (100), 55 (33), 45 (22), 29 (70), 28 (73).

Preparation of 4,7-Dioxa-1,10-Decanediol

A three liter, 3-necked flask equipped with a mechanical stirrer and a reflux condenser was purged with argon and charged with 1 liter of THF. $LiAlH_4$ (63g, 2.3 mole) was added to the THF gradually with stirring. After allowing the mixture to cool, 500 ml of a solution of Bis (2-carboethoxyethoxy)ethane (227g, 0.866 mole) in THF was added dropwise with good stirring via an additon funnel. After the addition the reaction mixture was stirred overnight. A 1:1 solution of H_2O: THF was added dropwise so as to destroy the excess hydride. The re-

action mixture was then poured into 10% H_2SO_4 (the final mixture must be acidic) producing two layers. The upper THF layer was separated and $MgSO_4$ was added, forcing out another aqueous layer. The THF layer was concentrated and the residue taken up in $CHCl_3$ to form another two layers. The $CHCl_3$ layer was dried with $MgSO_4$ and concentrated to give a viscous liquid. All aqueous layers were then combined and continuously extracted overnight with $CHCl_3$. The $CHCl_3$ was dried and concentrated to yield a colorless viscous liquid. The two viscous liquids were combined and distilled under vacuum to yield 105g (68%) of a fraction boiling at 132-135° (0.1 mm). nmr δ 1.55-2.03 (five line multiplet, 4H), 3.48-4.03 (multiplet, 14H), IR ($CHCl_3$) 3670 (w), 3630 (m), 3470-3490 (s), 2950 (s), 2930 (s), 2880 (s), 1140-1070 (s); mass spectrum m/e (rel. intensity), 179 (0.29, M+1), 148 (2.28), 129 (2.56), 121 (3.23), 120 (1.89), 104 (9.50), 103 (10.12), 89 (26.33), 86 (9.71), 75 (13.35), 61 (10.73), 59 (99.70), 58 (54.15), 57 (26.46), 45 (77.99), 41 (31.93), 31 (100.00).

Preparation of the Ditosylate of 4,7-Dioxa-1,10-decanediol

4,7-Dioxa-1,10-decanediol (41.5g, 0.233 mole) in 200 ml of pyridine was added to a 500 ml 3-necked flask which was equipped with a mechanical stirrer. An Erlenmeyer flask containing p-toluenesulfonyl chloride (102g, 0.537 mole) was attached to one neck of the flask with gooch tubing. The diol solution was cooled to about 0° and the p-toluenesulfonyl chloride was added gradually over a two hour period. When the addition was complete the reaction was stirred for an additional 4 hours at 0°. The reaction mixture was then poured onto ice and about 200 ml of cold water was added causing the product to precipitate. The product was suction filtered, washed three times with water and allowed to air dry. When dry it was washed with hexane, allowed to air dry again and then dried under vacuum

to constant weight. The yield was 105g (93%) of a white powder that smelled slightly of pyridine. nmr ($CDCl_3$), δ 1.67-2.10 (5 line multiplet, 4H), 2.43 (s, 6H), 3.42 (s, 4H), 3.45 (t, 4H), 4.10 (t, 4H), 7.29 (d, 4H), 7.74 (d, 4H).

Preparation of Benzo-14-Crown-4

A solution of catechol (6.04g (0.0549 mole) in 145 ml of n-butanol was added to a 500 ml, 3-necked flask equipped with a mechanical stirrer and a reflux condenser on top of which was a gas inlet tube. NaOH pellets (4.6g, 0.11 mole) were added and the entire system was flushed with nitrogen. An Erlenmeyer flask containing the ditosylate of 4,7-dioxa-1,10-decanediol (27.1g, 0.0558 mole) was attached to one of the necks with gooch tubing. The catechol-NaOH mixture was then stirred and gentle heating was applied while keeping the system under a static nitrogen atmosphere. Eventually the reaction mixture turned milky. Gentle heating and stirring was continued for about ten more minutes. The ditosylate was then added in one portion through the gooch tubing. The gooch tubing was replaced by a glass stopper and the heat was increased so as to reflux the mixture. After a short time a large precipitate, presumably sodium tosylate, appeared. Heating and stirring were continued for about 20 hours. After cooling, the reaction mixture was taken up in ether and the salts were removed by suction filtration. The ether and n-butanol were removed by rotary evaporation and the residue was taken up in ether and filtered. The ether solution was then extracted with a 5% solution of KOH in water until the water layer was almost colorless. The ether layer was dried with $MgSO_4$, concentrated and finally distilled under vacuum to give 6.46g (46.8%) of a clear colorless liquid at 120-130° (0.1 mm). nmr (CCl_4) δ 1.65-2.07 (5 line multiplet,

4H), 3.53 (s, 4H), 3.67 (t, 4H), 4.03 (t, 4H), 6.82 (s, 4H); IR 3060 (w), 2940-2850 (s), 2800 (w), 1590 (m), 1490 (s), 1465 (s), 1450 (s), 1420 (m), 1370 (m), 1345 (m), 1300-1190 (s), 1250-1140 (s), 980-945 (s) cm^{-1}; mass spectrum m/e (rel. intensity), 253 (6.60, M^+), 252 (38.41, M^+), 168 (9.34), 151 (15.05), 150 (97.63), 123 (10.05), 122 (33.87), 121 (100.00), 110 (37.28), 109 (36.21), 103 (6.69), 95 (5.63), 94 (6.41), 91 (7.31), 89 (5.20), 85 (12.64), 81 (15.52), 80 (15.11), 77 (9.22), 73 (9.69), 71 (6.25), 65 (7.34), 64 (7.05), 59 (18.68), 58 (8.84), 57 (18.68), 53 (7.52), 52 (16.48), 45 (26.00), 44 (5.88), 43 (17.24), 42 (17.29), 41 (69.99), 39 (16.36), 32 (16.98), 31 (22.09), 29 (20.27), 28 (58.62), 27 (18.12). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.67; H, 7.94. Found: C, 66.56; H, 7.97.

Preparation of Dibenzo-28-Crown-8

The dark brown semisolid pot residue (8.9g) from a benzo-14-crown-4 distillation (prepared from 0.264 mole of catechol) was chromatographed on 150g of alumina using benzene as the eluent. The first five fractions (ca. 75 ml each) were evaporated to yield 0.90 of a yellow solid. Recrystallization from isooctane followed by washing with hexane gave 0.76g (1.1%) of white crystals, m.p. 107.5-108.5. nmr ($CDCl_3$) δ 1.80-2.28 (5 line multiplet, 8H), 3.60 (s, 8H), 3.68 (t, 8H), 4.07 (t, 8H), 6.88 (s, 8H); mass spectrum m/e (rel. intensity), 506 (2.23, M+2), 504 (33.57, M^+), 252 (19.43), 191 (24.39), 163 (28.21), 151 (85.38), 150 (94.24), 143 (31.13), 123 (32.81), 122 (21.34), 121 (77.53), 110 (25.53), 109 (32.04), 103 (33.61), 88 (27.63), 59 (38.71), 57 (25.34), 45 (57.00), 43 (39.02), 41 (100.00), IR 3060 (w), 3040 (w), 2950-2910 (m), 2870 (s), 1495 (s), 1465 (m), 1450 (m), 1250-1240 (s), 1230-1200 (m), 1120-1110 (s) cm^{-1}. Calculated for $C_{28}H_{40}O_8$: C, 66.67; H, 7.94. Found: C, 66.78; H, 8.00.

Preparation of the Benzo-14-Crown-4 Complex of Lithium Bromide

Lithium bromide (1.12g, 12.9 mmole) was dissolved in about 50 ml of anhydrous ether. Benzo-14-crown-4 (3.21g, 12.7 mmole) in 20 ml of ether was added dropwise to the LiBr solution with rapid stirring. A white solid precipitated immediately upon adding the crown. After the addition, the solid was suction filtered and washed with ether to yield 4.2g (98%) of crude complex. Recrystallization of 2.5g of the crude produce from THF afforded 1.2g of white powdery crystals, m.p. 237-241.